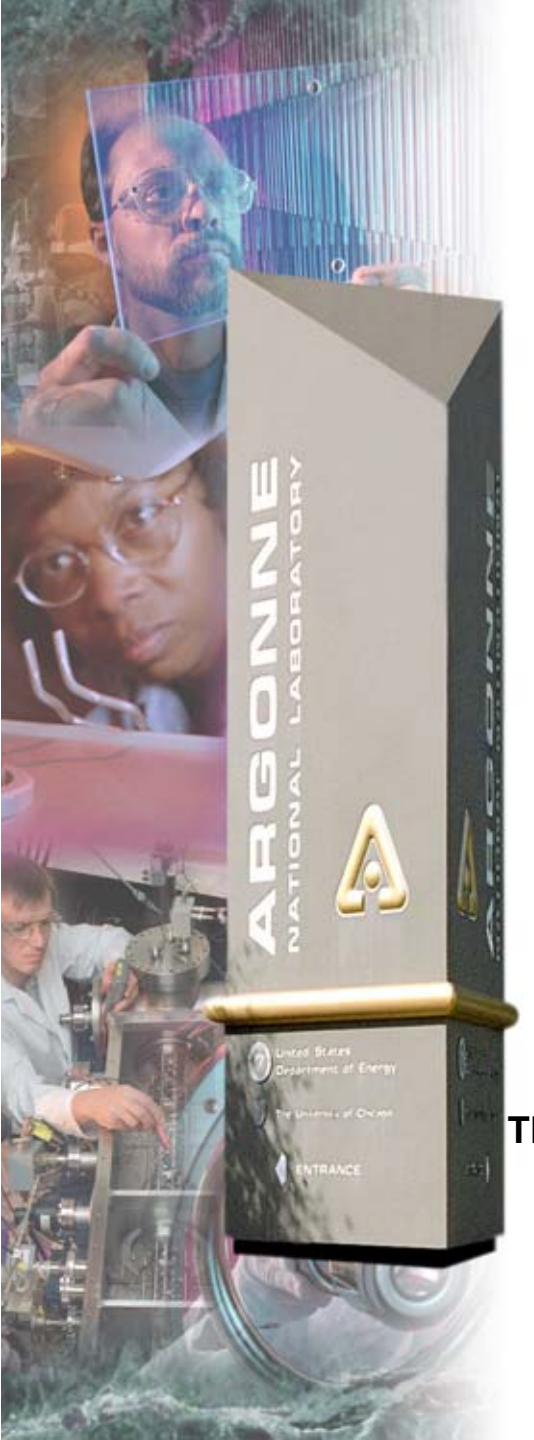


Water gas shift catalysis

Theodore Krause, Razima Souleimanova,
John Krebs, and Mario Castagnola

Electrochemical Technology Program
Argonne National Laboratory

May 24-27, 2004

This presentation does not contain any proprietary or confidential information

Hydrogen, Fuel Cells, and Infrastructure Technologies
Office of Energy Efficiency and Renewable Energy
U.S. Department of Energy

Objectives

- **To develop advanced water-gas shift (WGS) catalysts to meet the DOE performance requirements**
  - Compared to Cu-Zn and Fe-Cr WGS catalysts, these new catalysts will be
    - more active (higher turnover rates)
    - less prone to deactivation due to temperature excursions
    - more structurally stable (able to withstand frequent cycles of vaporizing and condensing water)
    - more resistant to sulfur poisoning
  - Improve our understanding of reaction mechanisms, catalyst deactivation, and sulfur poisoning
  - Define operating parameters (e.g. steam:carbon ratios, temperature, gas hourly space velocities (GHSV), catalyst geometry) to optimize catalyst performance and lifetime

Budget, technical barriers and targets

- **FY04 Funding: $600K**
- **Technical barriers**
  - A. Fuel Processor Capital Costs
  - G. Efficiency of Gasification, Pyrolysis, and Reforming Technologies
  - Z. Catalysts
  - AB. Hydrogen Separation and Purification
- **Technical targets for water gas shift catalysts**
  - gas-hourly space velocity (GHSV) ≥ 30,000 h^{-1}
  - CO conversion ≥ 90% and selectivity ≥ 99%
  - lifetime > 5000 h
  - cost <$1/$kW_e$

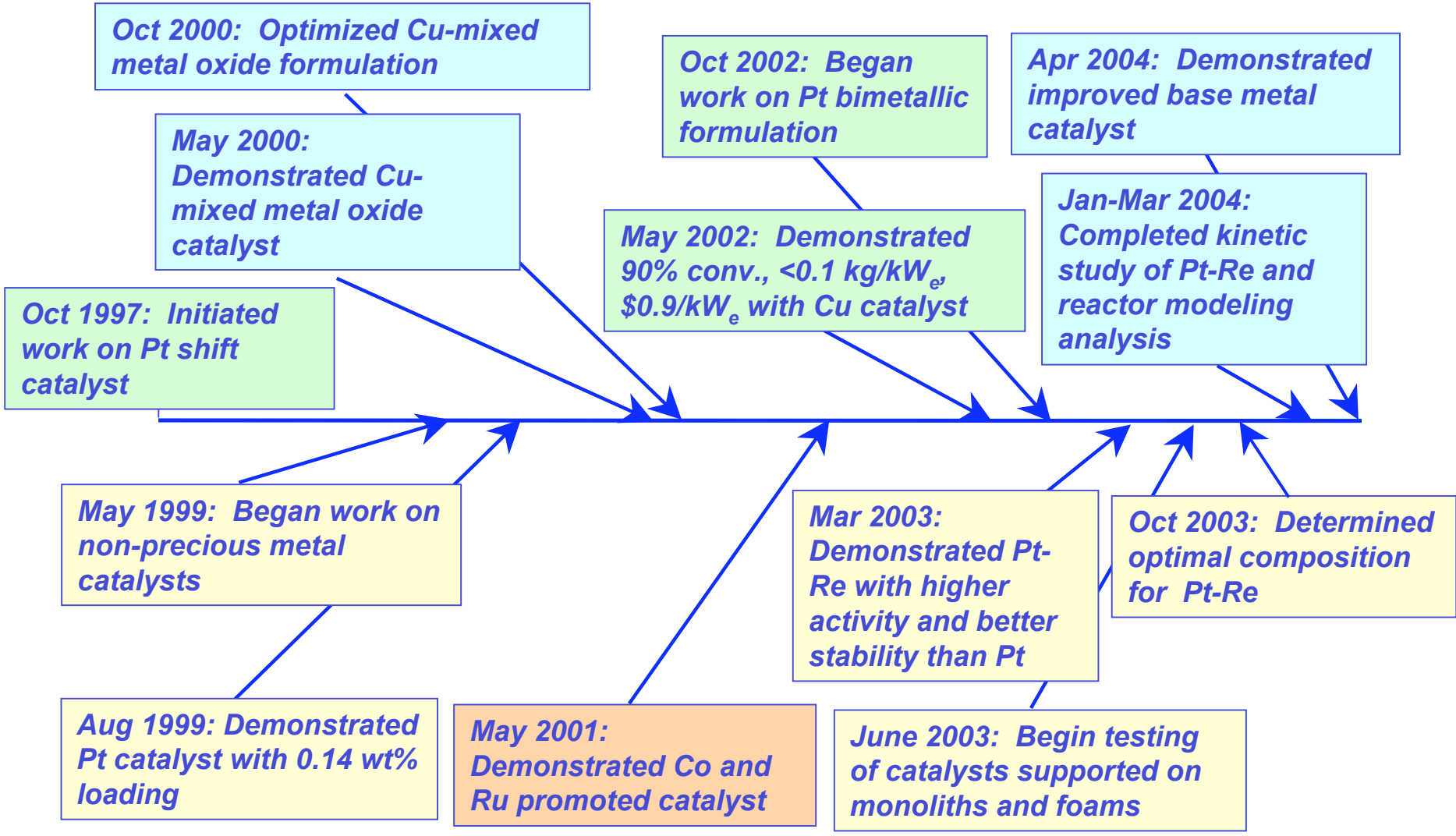
Approach

- Identify metal(s) and oxide combinations which promote one or more elementary reaction steps (e.g. CO oxidation, H_2O dissociation, formate/formyl decomposition) involved in the water-gas shift reaction
- Evaluate the water-gas shift activity of these materials in a microreactor system
- Use characterization techniques (e.g. X-ray spectroscopy, temperature-program reduction (TPR), and electron microscopy) to identify factors needed to improve WGS activity or to minimize catalyst deactivation
- Develop kinetic model to predict catalyst performance for reformer operating parameters

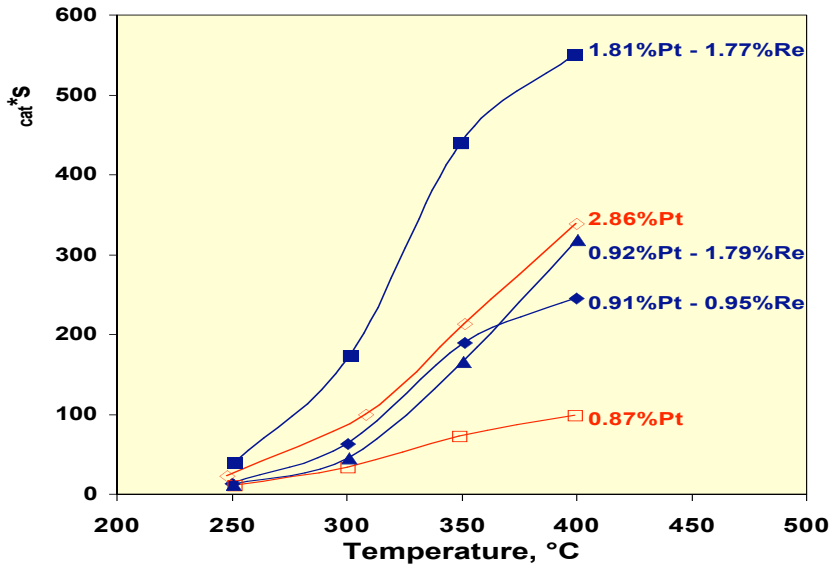
Project safety

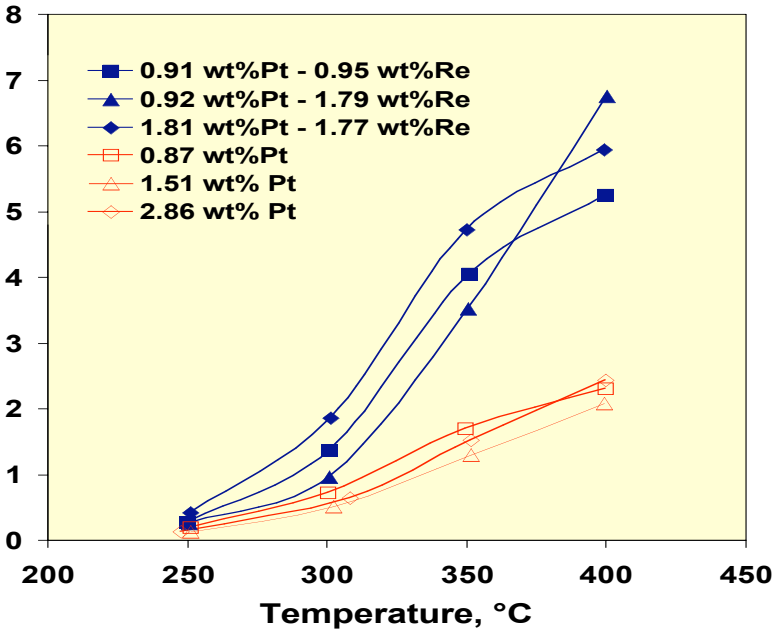
- Internal safety reviews are performed for all aspects of this project to address ESH issues
  - Catalyst synthesis
    - Synthesis procedures are performed in fumehoods to exhaust vapors of powders and solvents
    - Waste chemicals are collected and disposed of through the Laboratory's Waste Management Operations
  - Microreactor systems
    - Located in fumehoods
    - Equipped with safety interlocks that shut the system down if excessive temperature or pressure is sensed or the fumehood ventilation fails
- Safety reviews are updated and renewed annually

Project timeline



Addition of Re improves performance of Pt-ceria catalyst





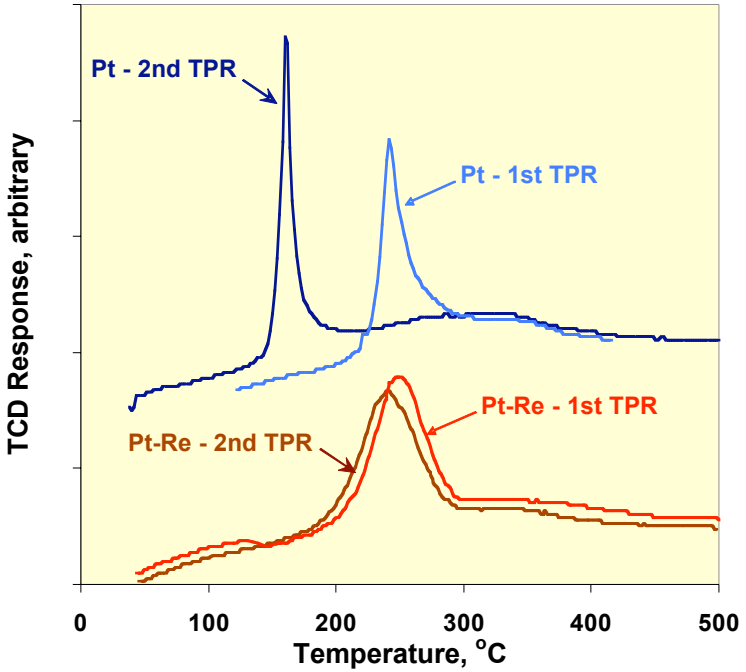
Rate Equation: $\exp(-E_a/RT)*CO^a*H_2O^b*H_2^c*CO_2^d$

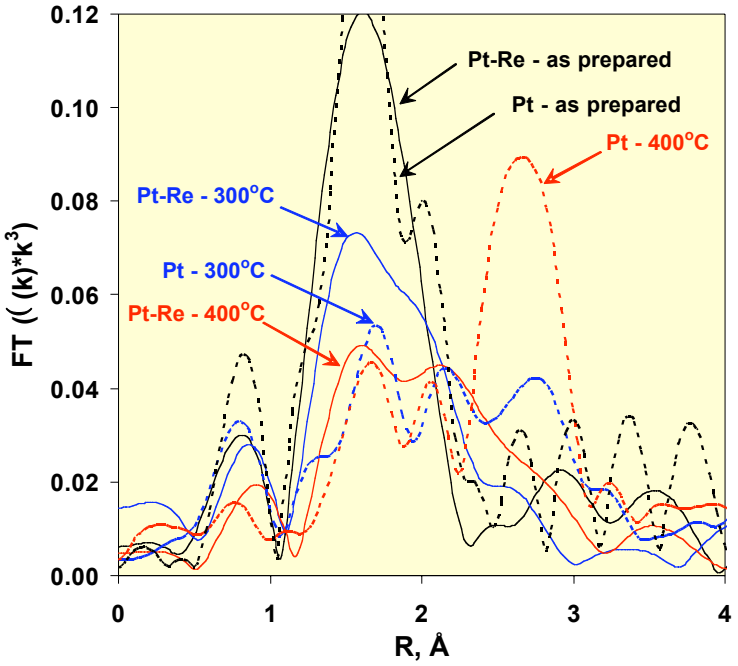
	E_a (kcal/mol)	a	b	c	d
Pt-Re	16	0	0.40	-0.58	-0.17
Pt*	11	0	0.5	-1	-0.5

*Ref: T. Bunluesin et al. Appl. Catal. B, 15 (1998) 107-114.

TPR and extended X-ray absorption fine structure (EXAFS) analysis suggests that Re stabilizes Pt

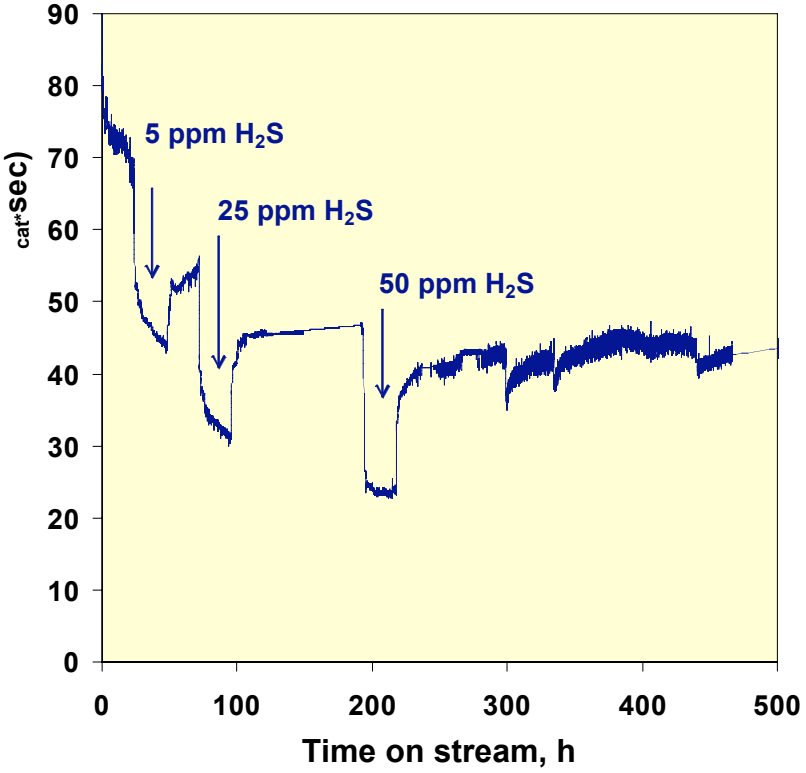
- For Pt, shift in reduction peak to lower temperature is indicative of particle growth
- For Pt-Re, no change in reduction profile
- More Pt-Pt bond formation in Pt than Pt-Re after 100+ h on stream at 400°C



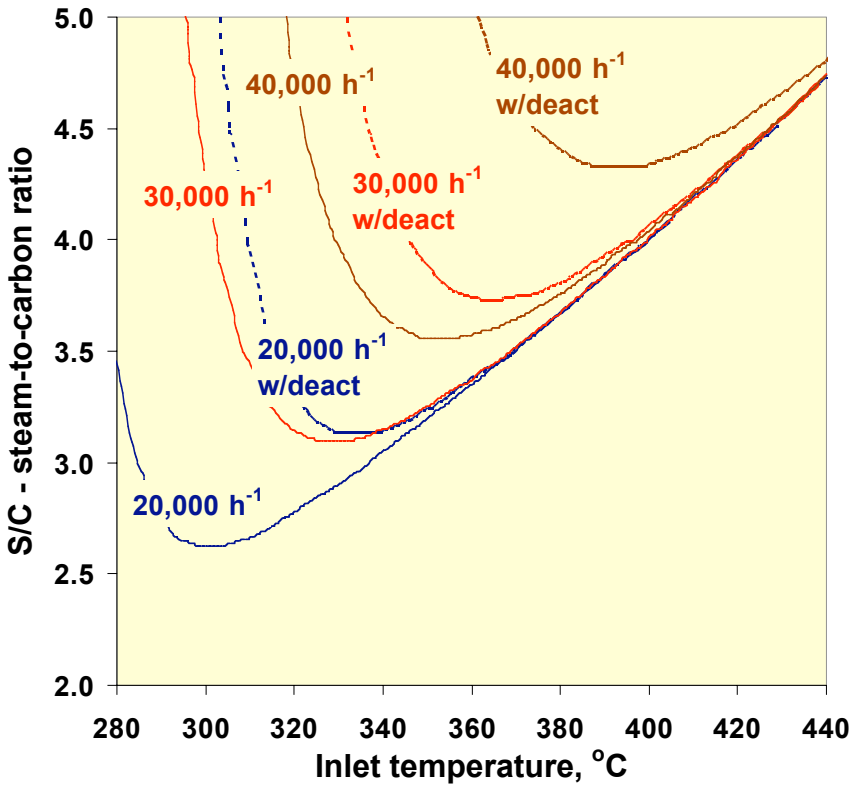


Even with deactivation, Pt-Re catalyst should be able to meet GHSV target

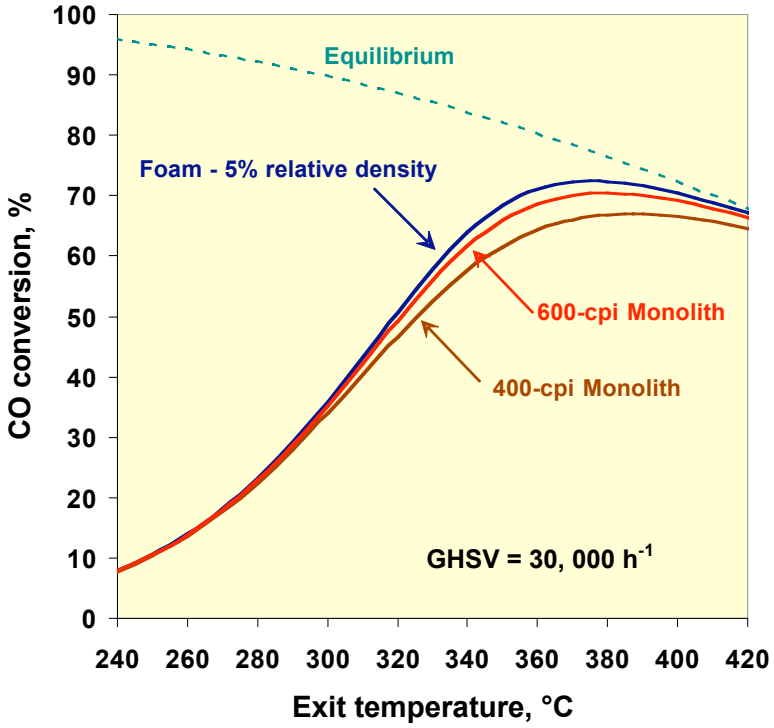
- Pt-Re lost about 50% of its initial activity during the first 250 hours, but the activity then stabilized

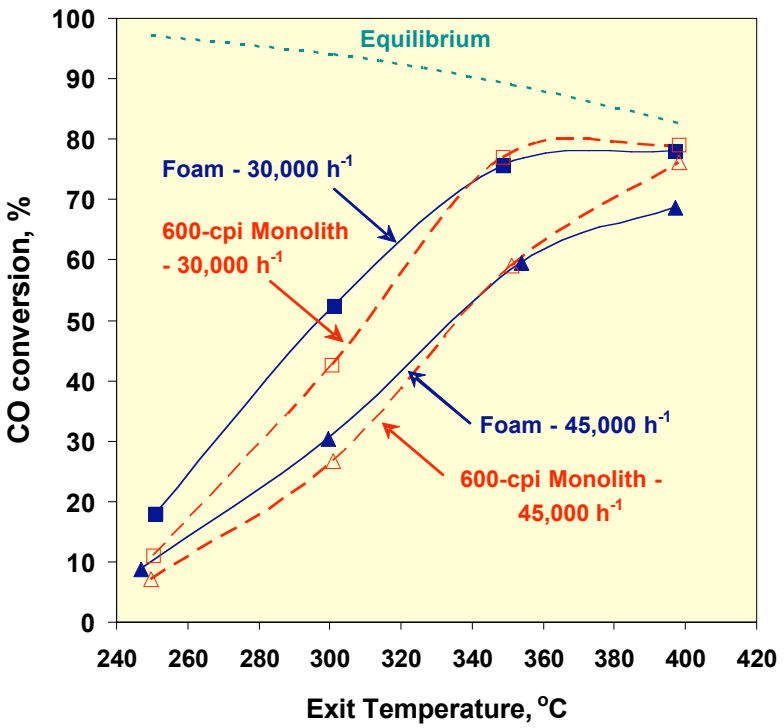


- Modeling study shows that 1% CO can be achieved even with deactivation if the temperature and S/C ratio are increased



Optimal geometric support for WGS catalyst - foam or monolith?

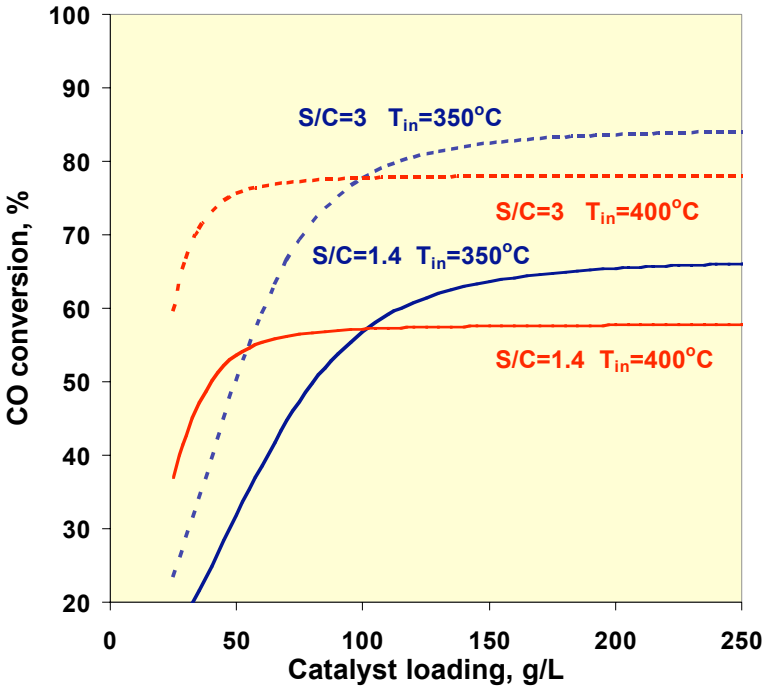


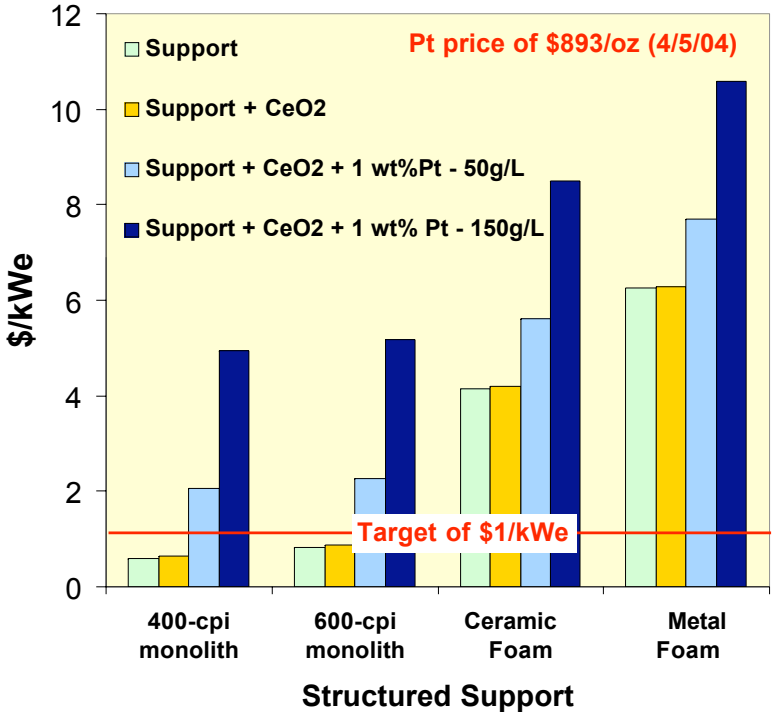


- **Both modeling and experimental studies show that there may be a slight benefit to using a foam as a support**
- **However, the monolith is the preferred support based on cost and production capacity**

Even with the higher activity of the Pt-Re, still higher activity is needed to meet the cost targets

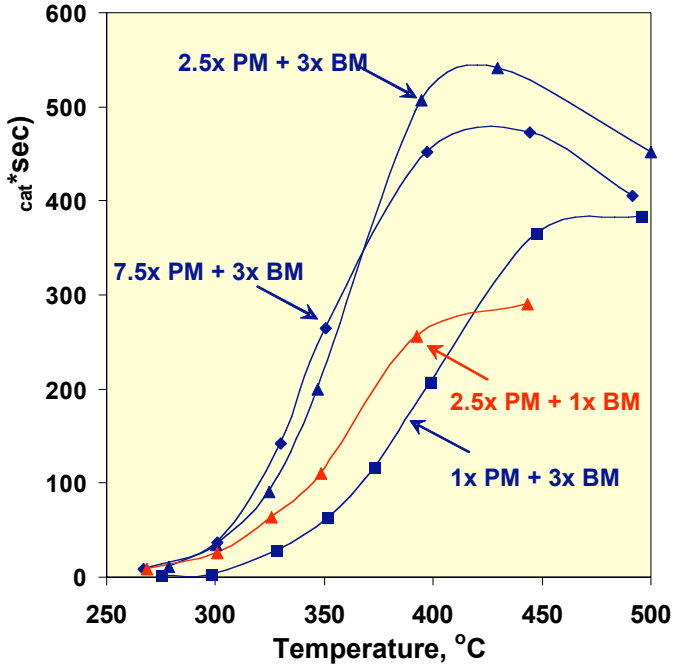
- Modeling studies suggest that the optimal catalyst loading on the structured support is 50-150 g/L
- The \$1/kW$_e$ target is tough to achieve

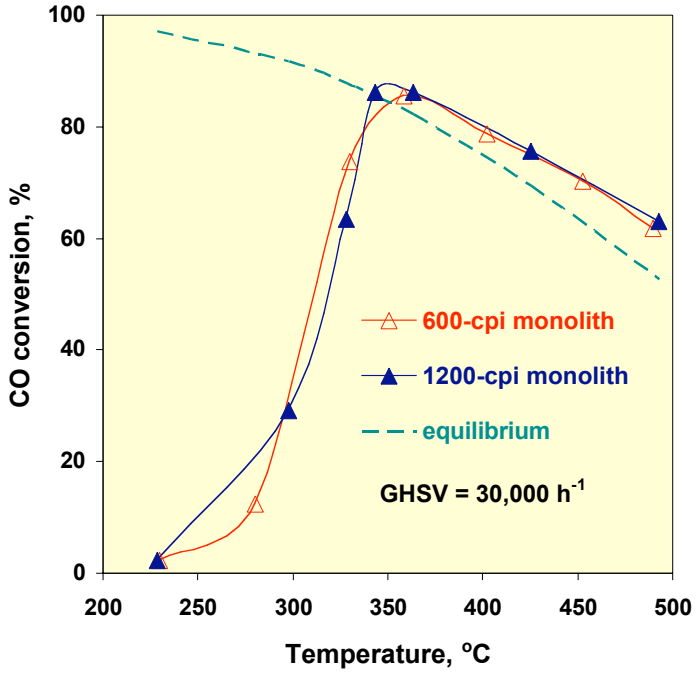




We are investigating less-costly precious metal bimetallic catalysts

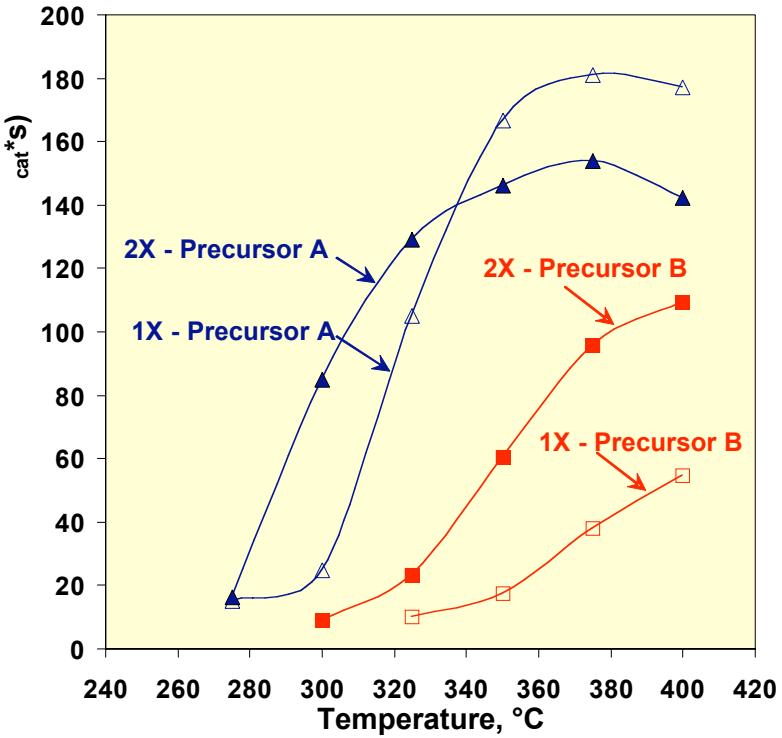
- A combination of a precious metal (PM)-base metal (BM) has been identified that exhibits higher WGS activity than either the PM or BM
- The equilibrium-predicted CO conversion is achieved at a GHSV of 30,000 h^{-1} at >340°C
- Long-term stability is yet to be verified

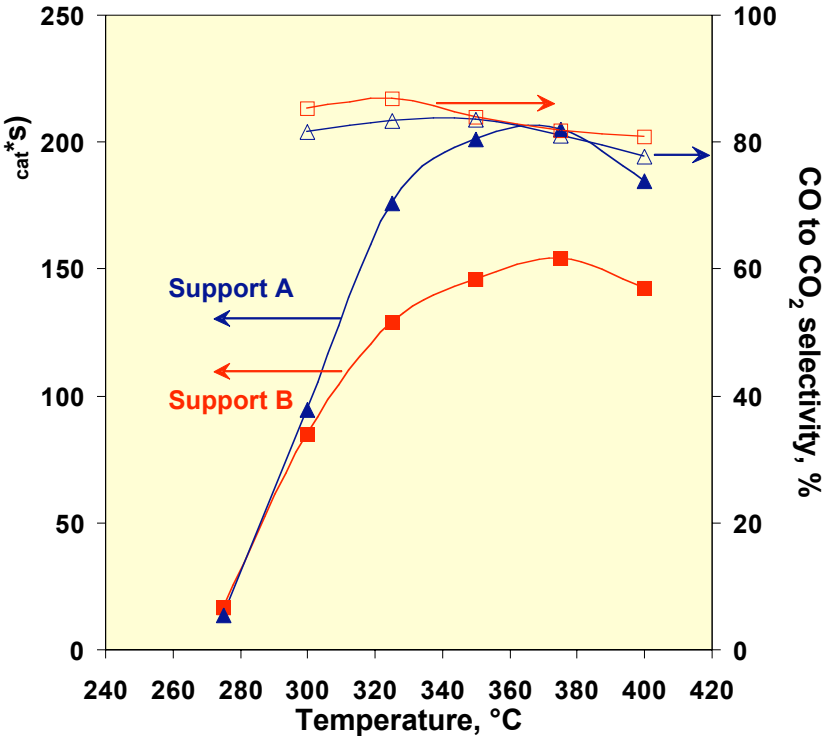




Base metal WGS catalysts may also be possible

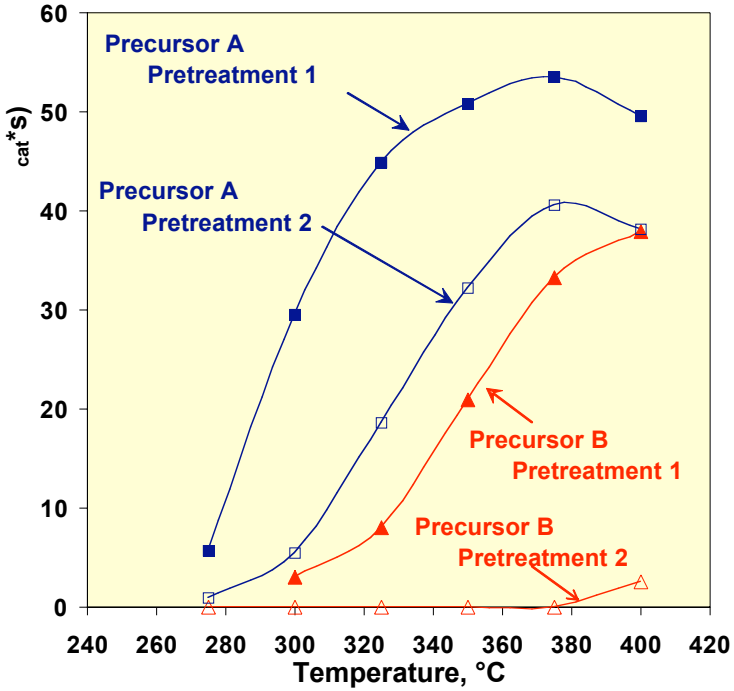
- The choice of precursor and oxide support were critical factors for optimizing activity
- The catalyst promotes methanation; however,
- The selectivity of CO to CO_2 does not depend on the precursor or support

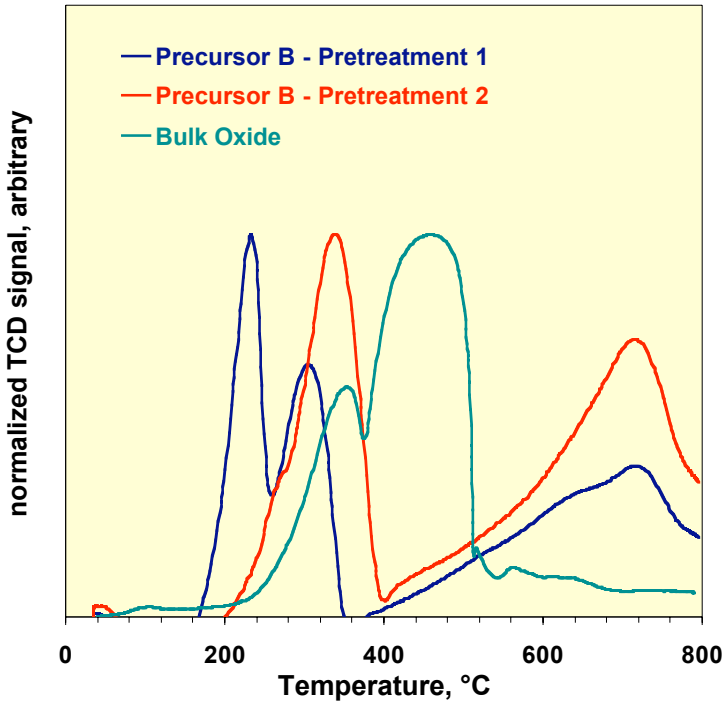




A critical factor for the base metal catalyst is to prevent formation of the oxide and surface interactions

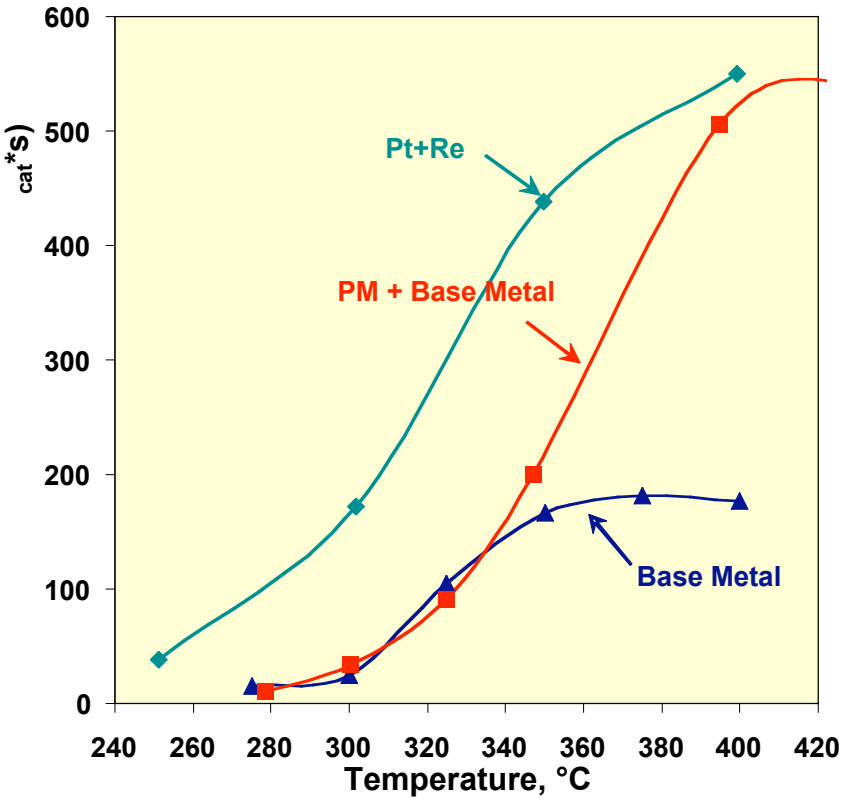
- Pretreatment has a significant influence on catalyst activity
- The most active catalysts have a reduction peak at ~200°C
- The reduction peak at ~700°C is indicative of metal-support interaction





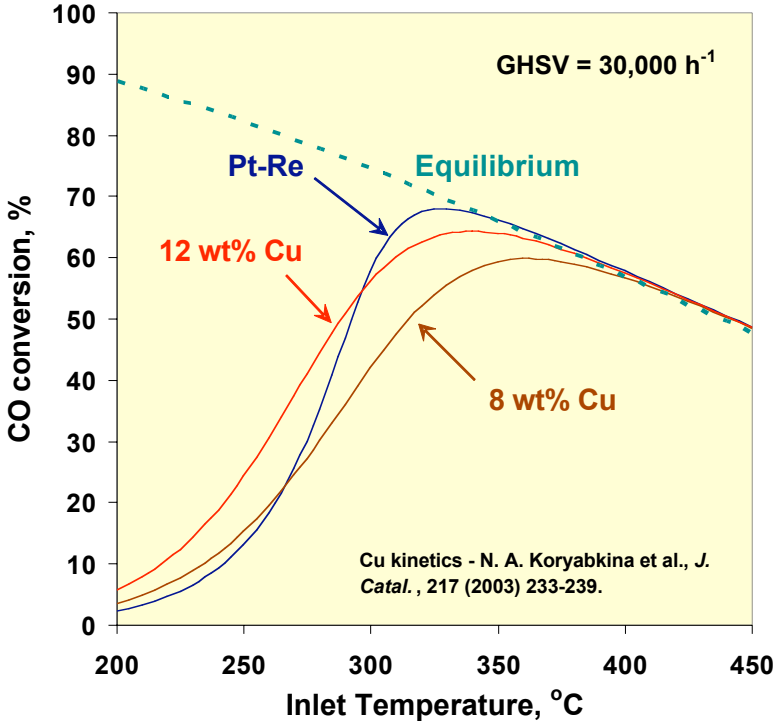
Comparing the three types of WGS catalysts

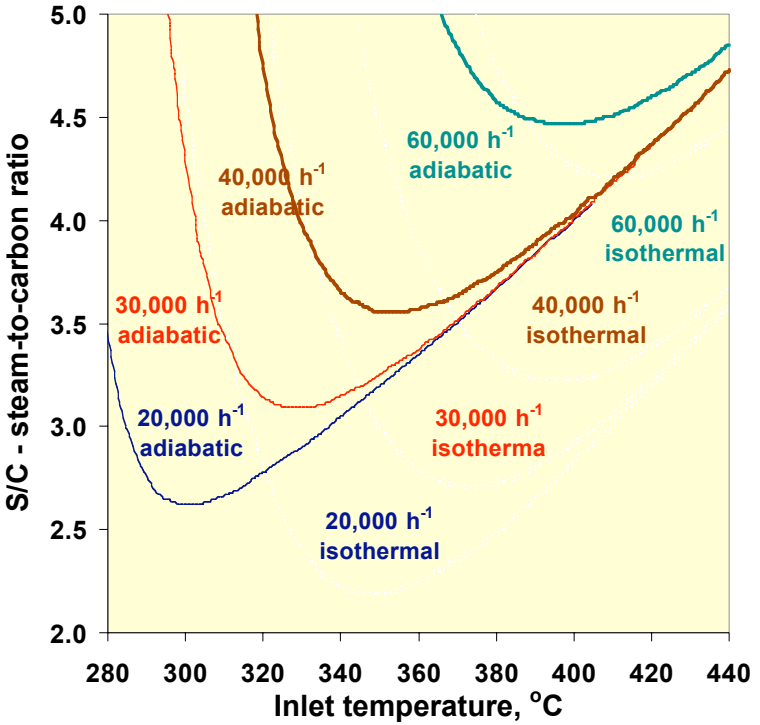
- **Pt-Re**
  - Very active shift catalyst
  - Good stability
  - High Cost
- **PM + Base Metal**
  - Good shift activity
  - Less costly than Pt-Re
  - Stability not yet established
- **Base Metal**
  - Less active than both Pt-Re and PM + Base metal catalysts
  - Methanation and stability are yet to be addressed
  - Lowest cost



Can we avoid low temperature shift for on-board reforming?

- Modeling studies show that the activity of Pt and Cu catalysts decreases significantly below 300°C
- Pt-Re can achieve 1% CO at >300°C at GHSV ≥30,000 h^{-1}





Interactions and collaborations

- University of Alabama (Prof. Ramana Reddy) to characterize shift catalysts using SEM, TEM, and XPS
- Non-disclosure agreement (NDA) with Catalytica Energy Systems to evaluate new shift catalysts
- Provided samples for evaluation
  - Toyota
  - Nissan
  - Süd-Chemie, Inc.

Response to reviewers' comments from FY03

- Monolith work should be given priority
- Improve durability (longer-term endurance testing is needed)
- Better performance from non-precious metal catalysts
- Are low temperature catalysts feasible for on-board fuel processing?

Milestones

Milestone	Date
Determine the optimal operating conditions for the water-gas shift reactor	01/04
Determine the optimal bimetallic formulation for the Pt-based shift catalyst	05/04
Complete the assessment of the feasibility of a low temperature non-precious metal catalyst to meet the DOE targets	05/04
Demonstrate ≤1% CO out using structured catalyst(s) for >500 h	09/04

Future work

- **For bimetallic precious metal-base metal and base metal catalysts**
  - Optimize formulation to increase activity and minimize methanation
  - Improve our understanding of reaction mechanisms
- **To improve catalyst durability and minimize deactivation**
  - Conduct characterization studies of spent catalysts to further understand deactivation mechanisms
  - Conduct long-term tests of improved catalyst formulations
- **Address catalyst issues identified in "FASTER" Program**
  - Catalyst deactivation and structural stability issues (i.e., effect of frequent and rapid startup)
  - Obtain performance data as a function of operating parameters to develop kinetic models